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(54) PURIFICATION OF PHOSPHORIC ACID SOLUTION

(57)Abstract:
PURPOSE: To remove arsenic in phosphoric acid liquid to 0.01ppm.
CONSTITUTION: In the method for removing arsenic in the phosphoric acid liquid as a sulfide by reacting the arsenic in the phosphoric acid liquid with hydrogen sulfide gas, the hydrogen sulfide gas in a weight of 30-150 times that of the arsenic in the phosphoric acid liquid is preliminarily dispersed in the phosphoric acid liquid at 30-80°C to react the arsenic with the hydrogen sulfide gas, followed by adsorption-removing the produced sulfide compound in an active carbon tower filled with coal active carbon.

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* NOTICES *

3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] In the approach of making the arsenic in phosphoric acid liquid reacting with hydrogen-sulfide gas, and removing the arsenic in this phosphoric acid liquid as a sulfide The purification method of the phosphoric acid liquid with which it is characterized by carrying out adsorption treatment of the part for the sulfide which is a resultant in the activated carbon filter filled up with activated carbon from coal after temperature distributes beforehand and makes 150 times [30 times to] as many hydrogen-sulfide gas as this react in a weight ratio to a part for the arsenic in this phosphoric acid liquid into the phosphoric acid liquid of 30-80-degreeC.
[Claim 2] The purification method of the phosphoric acid liquid according to claim 1 this whose activated carbon is granular charcoal.
[Claim 3] The purification method of the phosphoric acid liquid according to claim 1 whose concentration of this phosphoric acid liquid is 35 - 56 % of the weight as 2OP5 concentration.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the approach of removing a part for the arsenic of the minute amount contained in phosphoric acid liquid, in more detail about the purification method of phosphoric acid liquid.
[0002]
[Description of the Prior Art] Although there are phosphoric-acid-by-dry-process liquid and phosphoric-acid-by-wet-process liquid as phosphoric acid liquid The harmful nature at the time of using it as the pollution problem, the food, and the object for physic at the time of using it as a finishing agent in any case, Since a high grade article is required in case it uses as an electronic ingredient, the demand of arsenic removal is increasing increasingly and the arsenic content in phosphoric acid liquid is the situation that the thing of further a low content is required, below the 0.05 weight ppm (all ppm express weight ppm henceforth) in recently in the future in recent years. Generally the approach of making react with the compound (for these to be called a fusibility sulfide in this invention) which generates hydrogen-sulfide gas, and usually carrying out precipitation removal as an arsenic sulfide under acid conditions, such as a hydrogen sulfide or sodium sulfide, sulfuration potash, an ammonium sulfide, a sodium hydro sulfide, and ammonium hydrosulfide, is used

for removal for arsenic in phosphoric acid liquid. However, it was in the situation which cannot be removed to satisfaction until precipitation of the arsenic sulfide generated by this approach tends to become colloid nature, there is difficulty in separation from high concentration phosphoric acid liquid with high viscosity and it could respond to the specification that the above-mentioned arsenic content is severe.

[0003] It was remarkable as the arsenic content in phosphoric acid liquid became low, and especially this phenomenon appeared notably, when an arsenic content targetted phosphoric acid liquid several ppm or less, and arsenic removal was very difficult for it.

[0004] In order to aim at filterable amelioration of the arsenic sulfide precipitation which the elimination factor of arsenic improves and generates, the approach (Japanese Patent Publication No. 49-No. 37030 official report) which much researches are made, for example, adds a fusibility sulfide under existence of activated carbon, the method (JP,49-129696,A) of removing to coincidence the phosphoric acid root which also adds and contains a potassium compound further if it is in phosphoric acid by wet process, and arsenic, etc. are indicated.

[0005] Conventionally, it was required in a lot of [although the approach in which activated carbon is made to exist for arsenic removal is so much ineffective with granular charcoal / in order for considerable effectiveness to reduce the arsenic content of a certain thing below in for example, the 0.1 weight ppm in the phosphoric acid liquid which contains the organic substance especially with powder charcoal, for example, the phosphoric acid liquid by the wet method,] activated carbon. And in the case of the phosphoric acid liquid (for example, phosphoric acid liquid by the wet method) which contains the organic substance further, the removal for the organic substance became a ** rule, and the removal for arsenic was difficult. For this reason, it was accompanied by various problems on actuation, such as leakage of the activated carbon at the time of adding activated carbon quite so much, consequently performing elution for an impurity in activated carbon, and separation according to **.

[0006] These people etc. previously Phosphoric-acid-by-wet-process liquid, extract phosphoric acid liquid (the phosphoric acid which carried out extract purification and obtained phosphoric-acid-by-wet-process liquid with the organic solvent is said), The result of having repeated examination about removal of the arsenic contained in it for various phosphoric acid liquid, such as phosphoric-acid-by-dry-process liquid, It is very difficult to remove the arsenic in (1) phosphoric-acid liquid by the approach of well-known arsenic removal, i.e., the method of only adding and removing a hydrogen sulfide or a fusibility sulfide, to 0.05 ppm or less. (2) When the arsenic content in the phosphoric acid liquid in front of dearsenic is still lower, especially an arsenic content is very difficult for this inclination being remarkable and removing the arsenic in the phosphoric acid liquid behind dearsenic to 0.1 ppm or less in about 2.0 ppm or less. Moreover, by the approach of adding activated carbon with a hydrogen sulfide or fusibility arsenide on the occasion of arsenic removal, (3) arsenic removal, especially the organic substance are contained, for example, a certain amount of effectiveness shows the inclination as the above-mentioned (1) term and (2) terms with the same arsenic elimination factor of a certain thing to arsenic removal of phosphoric-acid-by-wet-process liquid or extract phosphoric acid liquid.

[0007] By the conventional approach of adding a hydrogen sulfide or a fusibility sulfide, in more detail the inclination of this arsenic elimination factor When the arsenic content obtained is the phosphoric acid liquid which is 10-20 ppm, in phosphoric acid by wet process usually, to 0.05-0.10 ppm When it is the phosphoric acid liquid whose arsenic content is 1 ppm, to the ability to fall less than to to 0.02-0.06 ppm (i.e., at least 0.1 ppm) in dry type or extract phosphoric acid Dry type, Also in wet and which phosphoric acid of an extract, it can fall only to about at most 0.7-0.9 ppm, but the rate of dearsenic is very bad. In order to gather an arsenic elimination factor, even if it uses powdered active carbon together, it cannot remove only to about 0.1 ppm. (Since activated carbon is moreover added quite so much in this approach, the problem on many actuation, such as elution of the impurity in activated carbon and leakage of the activated carbon in the case of filtration

separation, is derived by this.) that is By the well-known dearsenic approach, it was impossible for any approach to have reduced the arsenic content in phosphoric acid liquid to 0.01 ppm, and it was a technical level in the arsenic content that the rate of dearsenic is very bad especially in phosphoric acid liquid several ppm or less.

[0008] These people etc. note the point that an arsenic elimination factor changes with arsenic contents of phosphoric acid liquid, while groping for various the approaches of solving this problem previously. Although all could not remove the arsenic content behind dearsenic to 0.01 ppm or less by the well-known approach when the place which tried the approach of performing arsenic removal, and an arsenic content were low after adding powdery inorganic arsenide in phosphoric acid liquid The result referred to as being able to make an arsenic content to 0.01 ppm or less was obtained and proposed also about which phosphoric acid by carrying out minute amount addition of the inorganic arsenide (JP,58-46445,B).

[0009] However, although this approach was useful about removal of arsenic, it being necessary to newly add inorganic arsenide, processing of the sulfide containing a part for the arsenic made to process, etc. have the trouble which should be solved, and the further improvement was desired.

[0010]

[Means for Solving the Problem] Then, after this invention person etc. makes hydrogen-sulfide gas add and react to phosphoric acid liquid as a result of repeating research variously again about the reaction of hydrogen-sulfide gas and arsenic, and the adsorption treatment by activated carbon, by activated carbon, he finds out the approach of carrying out adsorption treatment of the resultant, and results in completion of this invention.

[0011] Namely, this invention makes the arsenic in phosphoric acid liquid react with hydrogen-sulfide gas, and is set to the approach of removing the arsenic in this phosphoric acid liquid as a sulfide. Temperature distributes beforehand 150 times [30 times to] as many hydrogen-sulfide gas as this in a weight ratio to a part for the arsenic in this phosphoric acid liquid into the phosphoric acid liquid of 30-80-degreeC. After making it react, it is the purification method of the phosphoric acid liquid characterized by carrying out adsorption treatment of the part for the sulfide which is a resultant in the activated carbon filter filled up with activated carbon from coal. Furthermore, the concentration of the phosphoric acid liquid which it tends to process moreover the activated carbon to be used is granular charcoal is the purification method of said phosphoric acid liquid which is 35 - 56 % of the weight (all %s express weight % below) as 2OP5 concentration.

[0012] This invention is further explained to a detail. In case arsenic is removed, the compound which generates a hydrogen sulfide under acid conditions has many compounds like the above-mentioned, but when the effect on the phosphoric acid liquid which it is going to process is taken into consideration, hydrogen-sulfide gas without the effect of a cation is suitable.

[0013] As an addition of this hydrogen-sulfide gas, they are 60 times to 100 times still more preferably 50 times to 120 times preferably 30 times to 150 times (As:H2S=1:30-150) in a weight ratio to a part for the arsenic in phosphoric acid. If the addition of hydrogen-sulfide gas is 30 or less times, according to this invention person's etc. research, the fall of dearsenic cannot be caused and arsenic concentration in the phosphoric acid liquid after processing cannot clear 0.01 ppm or less. Moreover, if it is 150 or more times, the problem of the corrosion of the metallic material by hydrogen-sulfide gas to be used also has the effectiveness of dearsenic, and it is not desirable while it causes the fall of the life of activated carbon since [which is a problem] activated carbon is adsorbed in hydrogen-sulfide gas although there is nothing.

[0014] Thus, about the removal for arsenic in phosphoric acid, it is making the hydrogen-sulfide gas of a large excessive amount add to the theoretical value as a sulfide, and the effectiveness of this invention can be attained.

[0015] Dry type, wet, and which phosphoric acid liquid of an extract are sufficient as the phosphoric acid liquid with the effective approach of this invention. As concentration of the phosphoric acid liquid in this invention, it is 40 - 50% preferably 35 to 56% as 2OP5 concentration. At 35% or less of

2OP5 concentration, the capacity of the phosphoric acid liquid which it is going to process increases, it is not industrially suitable, and according to this invention person's etc. research, the effectiveness of dearsenic cannot be demonstrated enough, either. On the contrary, if it is 56% or more of 2OP5 concentration, since there is a rise of the viscosity of phosphoric acid liquid, the fall of the adsorption capacity to activated carbon is seen, and it is not suitable.

[0016] As a content of the arsenic in the phosphoric acid liquid which it is going to process, about several ppm are suitable. in the case of beyond it, the effectiveness of this invention can be proved enough, but economically, after performing dearsenic to about several ppm beforehand by the conventional approach, it is useful to use the approach of this invention and it is efficient -- certain **

[0017] moreover -- as reaction temperature (whenever [phosphoric acid solution temperature]) -- 30-80-degreeC -- it is 40-60-degreeC preferably. Below the temperature C of 30 degrees of the reaction of hydrogen-sulfide gas and arsenic is inadequate, and probably because the viscosity of phosphoric acid liquid rises further, the fall of the adsorption capacity to activated carbon is seen. In more than 80-degreeC, in order to maintain temperature, energy is needed, and it is not economical while there is a problem of the corrosion to the equipment by hydrogen-sulfide gas and it needs to make higher-class the quality of the material to be used.

[0018] as activated carbon -- a grain and powdered active carbon -- although a problem does not have either in the field of the effectiveness of this invention, it is it being able to reproduce easily and making the liquid which is going to fill up a column with and which it is going to process pass, and since the effectiveness is acquired, granular active carbon is suitable. As a class of activated carbon, although there are a coal system, a coconut husks system, a pitch system, and a charcoal system from the raw material source, a coal system is suitable, judging from the effectiveness of dearsenic.

[0019] Although the approach of this invention can be enforced by any method of the batch approach and a continuous magnetization method, the continuous magnetization method is usually easier for operation.

[0020] Hereafter, one suitable example of this invention is explained to a detail, referring to an attachment **** drawing. Drawing 1 is a flow sheet which shows one suitable mode of operation of this invention.

[0021] Phosphoric acid liquid 1 adds the hydrogen-sulfide gas 3 of the specified quantity by the mixer 2, and makes homogeneity distribute hydrogen-sulfide gas 3 in this phosphoric acid liquid. A mixer 2 has the desirable thing of a format which makes ultrashort time amount distribute hydrogen-sulfide gas to homogeneity in phosphoric acid liquid, for example, a line mixer etc. is suitable for it.

[0022] If it is the conditions to which especially the contact time of hydrogen-sulfide gas and phosphoric acid liquid, i.e., reaction time, is not limited, and vapor-liquid contacts homogeneity enough, it will be very good in a short time, for example, there will be especially no problem also per second.

[0023] Next, the phosphoric acid liquid 4 made to add and process hydrogen-sulfide gas is led to the activated carbon filter 5 which is a coal system and was filled up with granular active carbon, and the dearsenic phosphoric acid liquid 6 to which adsorption treatment of the sulfide is carried out is obtained.

[0024] As a particle size of granular charcoal in an activated carbon filter 5, although it is necessary to take into consideration the content for an impurity except the arsenic of the phosphoric acid liquid which an about (about 0.9 - 1.1mm of mean particle diameter) 0.4-2.0mm thing is suitable, and it is going to process as a dipping rate of phosphoric acid liquid in view of the pressure loss and adsorption effectiveness of a column, it is good to dip with 0.5 - 2.0 m/h extent. In addition, as physical properties of the activated carbon to be used, the activated carbon for the liquid phase generally marketed is enough, and if it is the thing of the physical properties of specific surface area of 900-1300m 2 / g by the BET adsorption method, the iodine amount of adsorption 900 - 1100

mg/g, pore volume 0.9 - 1.0 cc/g extent, there will be especially no limitation.
[0025]
[Example] Hereafter, an example and the example of a comparison explain the effectiveness of this invention concretely.
[0026] According to the flow of drawing 1 , it examined continuously using the phosphoric-acid-by-dry-process liquid of the presentation shown in example 1 table 1. In addition, test time was performed for 150 hours.
[0027]
[Table 1]

P_2O_5	42～43%
As	2.0 ～2.5ppm

[0028] After making the activated carbon filter (2.0m of tower diameters) which carried out 440 g/h addition of the hydrogen-sulfide gas, and subsequently filled up 3.5t [/h] phosphoric acid liquid with a temperature of 50-53 degrees C with 3 15m (Oriental Calgon Corp. make, trade name F-400) of granular active carbon of a coal system pass using a line mixer, when the arsenic in phosphoric acid liquid was analyzed every 10 hours, all arsenic concentration was 0.01 ppm or less.
[0029] As a result of performing the completely same actuation as an example 1 except not adding example of comparison 1 hydrogen-sulfide gas, the arsenic concentration in phosphoric acid liquid was 0.10-0.15 ppm in the measurement in every 10 hours.
[0030] 40 g/h addition of the arsenic sulfide gas was carried out by the same approach as example of comparison 2 example 1, and the same trial was performed. The arsenic concentration in phosphoric acid liquid was 0.10-0.13 ppm in the measurement in every 10 hours.
[0031] Using the phosphoric acid liquid obtained with the wet method shown in example 2 table 2, the continuous corrosion test was carried out like the example 1. Continuous corrosion test time amount was carried out for 120 hours.
[0032]
[Table 2]

P_2O_5	50～53%
有機物 (as C)	60～80ppm
As	0.05～0.10ppm

[0033] After making the activated carbon filter (2.0m of tower diameters) which carried out 25 g/h addition of the hydrogen-sulfide gas, and subsequently filled up 5.0t [/h] phosphoric acid liquid with a temperature of 40-45 degrees C with 3 15m (Oriental Calgon Corp. make, trade name F-400) of granular active carbon of a coal system pass using a line mixer, when the arsenic in phosphoric acid liquid was analyzed every 10 hours, all arsenic concentration was 0.01 ppm or less.
[0034] As a result of performing the completely same actuation as an example 2 for the temperature of example of comparison 3 phosphoric-acid liquid 20-25-degreeC and except it, the

arsenic concentration in phosphoric acid liquid was 0.04-0.07 ppm in the measurement in every 10 hours.
[0035] When the same experiment as an example 2 was completely conducted except having changed example of comparison 4 granular active carbon to coconut shell charcoal (diamond SOBUW made from 3 ****** Co.), the arsenic concentration in phosphoric acid liquid was 0.05-0.08 ppm in the measurement in every 10 hours.
[0036]
[Effect of the Invention] This invention can remove arsenic to 0.01 ppm or less, without adding the new inorganic arsenide which had to be used conventionally, and is very useful on industry.
[0037] the purification approach of the phosphoric acid liquid of this invention -- like the above-mentioned -- 1 -- it is also the description of this invention that hydrogen-sulfide gas is added to the phosphoric acid liquid which it is going to process beforehand, and it comes out enough, is by the gas-liquid-contact process made to distribute in liquid and the adsorption process which consists of an activated carbon filter made to fill up with 2 activated carbon, and can remove with very easy approach and facility. moreover, this activated carbon filter 5 -- in addition, removal of the organic substance and decolorization of a product -- or -- in addition, removal for a heavy-metal metallurgy group etc. can be carried out to coincidence, is with the existing facility, and an activated carbon brand is subject to change -- it is -- it is also one of the descriptions of this invention that it can process by mixed use etc. Moreover, when newly installing the equipment in this invention separately, an installed cost can also respond very cheaply that what is necessary is just to form easy equipment.
[0038] the point that an arsenic content shows the effectiveness which boiled the approach of this invention very markedly to the well-known approach conventionally, and was excellent in the further dearsenic from phosphoric acid liquid several ppm or less should observe especially.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] The flow sheet Fig. showing an example of the equipment which was suitable in order to carry out this invention
[Description of Notations]
1 Phosphoric Acid Liquid
2 Mixer
3 Hydrogen-Sulfide Gas
4 Phosphoric Acid Liquid Processed by Hydrogen-Sulfide Gas
5 Activated Carbon Filter
6 DeArsenic Phosphoric Acid Liquid

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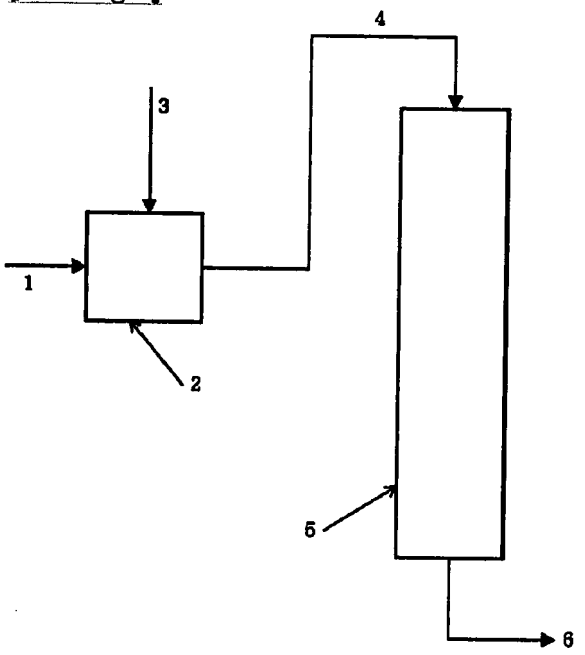
DRAWINGS

[Drawing 1]



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書誌

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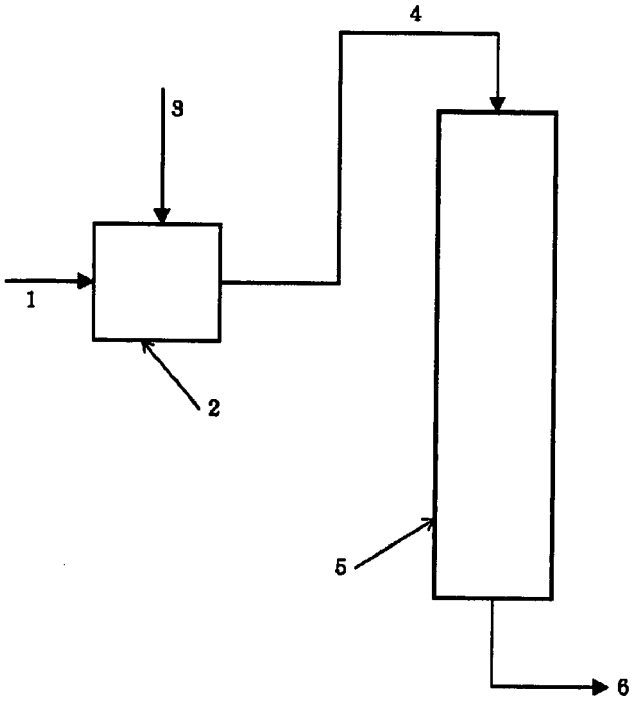
要約

(57)【要約】
【構成】 燐酸液中の砒素を硫化水素ガスと反応させて、該燐酸液中の砒素を硫化物として除去する方法において、温度が30～80℃の燐酸液中へ、燐酸液中の砒素分に対して重量比にて30倍～150倍の硫化水素ガスを予め分散し、反応せしめた後、石炭系活性炭を充填した活性炭塔にて、反応生成物である硫化物分を吸着除去する。
【効果】 燐酸液中の砒素を0．01ppmまで除去することができる。



請求の範囲

【特許請求の範囲】
【請求項1】燐酸液中の砒素を硫化水素ガスと反応させて、該燐酸液中の砒素を硫化物として除去する方法において、温度が30～80°Cの燐酸液中へ、該燐酸液中の砒素分に対して重量比にて30倍～150倍の硫化水素ガスを予め分散し、反応せしめた後、石炭系活性炭を充填した活性炭塔にて、反応生成物である硫化物分を吸着除去することを特徴とする燐酸液の精製法。
【請求項2】該活性炭が粒状炭である請求項1記載の燐酸液の精製法。
【請求項3】該燐酸液の濃度がP_2O_5濃度として35～56重量%である請求項1記載の燐酸液の精製法。

詳細な説明

【発明の詳細な説明】
【0001】
【産業上の利用分野】本発明は燐酸液の精製法に関するものであり、更に詳しくは燐酸液中に含まれる微量の砒素分を除去する方法に関するものである。
【0002】
【従来の技術および発明が解決しようとする課題】燐酸液には乾式燐酸液と湿式燐酸液とがあるが、いずれの場合も表面処理剤として使用する際の公害問題、食品や医薬用として使用する際の有害性、電子材料として用いる際に高純度品が要求されることなどから、近年、砒素除去の要求が益々高まっており最近では燐酸液中の砒素含有量は0．05重量ppm（以後ppmは全て重量ppmを表わす）以下、将来は更に低含有量のものを要求される情勢である。燐酸液中の砒素分の除去には通常、硫化水素または硫化ソーダ、硫化カリ、硫化アンモニウム、水硫化ソーダ、水硫化アンモニウムなどの、酸性条件下で硫化水素ガスを発生する化合物（本発明においてはこれらを可溶性硫化物と呼ぶ）と反応させ砒素硫化物として沈澱除去する方法が一般的に用いられている。然しこの方法では生成する砒素硫化物の沈澱が膠質性になりやすく、粘度の高い高濃度燐酸液からの分離には困難があり、上記砒素含有量の厳しい規格に対応し得る迄、満足に除去しえない状況であった。
【0003】特にこの現象は燐酸液中の砒素含有量が低くなるに従って著しく、砒素含有量が数ppm以

下の燐酸液を対象とした時顕著に現れ、砒素除去が極めて困難であった。
【0004】砒素の除去率の向上及び生成する砒素硫化物沈澱の濾過性改良を図るため、数多くの研究がなされており、例えば活性炭の存在下に可溶性硫化物を添加する方法(特公昭49－37030号公報)や、湿式燐酸にあっては更にカリウム化合物をも加えて含有する燐酸根と砒素を同時に除去する方法(特開昭49－129696号公報)などが開示されている。
【0005】従来、砒素除去の為に活性炭を存在させる方法は、粒状炭ではさほど効果はないが粉状炭では特に有機物を含む燐酸液、例えば湿式法による燐酸液において相当効果はあるものの砒素含有量を、例えば0.1重量ppm以下迄低下させるためには大量の活性炭を必要であった。そして更に有機物を含有する燐酸液(例えば湿式法による燐酸液)の場合には、有機物分の除去が律則となり、砒素分の除去は困難であった。このため活性炭をかなり多量に添加する必要があり、その結果、活性炭中の不純物分の溶出や濾別分離を行った際の活性炭の漏れなど操作上の種々の問題を伴っていた。
【0006】本出願人等は先に、湿式燐酸液、抽出燐酸液(湿式燐酸液を有機溶媒で抽出精製して得た燐酸を言う)、乾式燐酸液などの種々の燐酸液を対象としてその中に含まれる砒素の除去について検討を重ねた結果、公知の砒素除去の方法、即ち単に硫化水素または可溶性硫化物を添加して除去する方法では、(1)燐酸液中の砒素は0.05ppm以下迄除去することは非常に困難である。(2)更には、脱砒素前の燐酸液中の砒素含有量が低い場合、特に砒素含有量が、2.0ppm程度以下ではこの傾向が顕著で、脱砒素後の燐酸液中の砒素を0.1ppm以下迄除去することは極めてむつかしい。又、砒素除去に際し硫化水素または可溶性砒素化合物と共に活性炭を添加する方法では、(3)砒素除去、特に有機物を含有する、例えば湿式燐酸液や抽出燐酸液の砒素除去には、ある程度の効果はあるものの砒素除去率は上記(1)項及び(2)項と同様な傾向を示す。
【0007】この砒素除去率の傾向は更に詳しくは、硫化水素または可溶性硫化物を添加する従来の方法では、通常得られる砒素含有量が10～20ppmの燐酸液の場合、湿式燐酸では0.05～0.10ppm迄、乾式又は抽出燐酸では0.02～0.06ppm迄、即ち少なくとも0.1ppm以下には低下出来るのに対し砒素含有量が例えば1ppmの燐酸液の場合は乾式、湿式、抽出の何れの燐酸においてもせいぜい0.7～0.9ppm程度迄しか低下出来ず脱砒素率が非常に悪い。砒素除去率を上げる為に粉状活性炭を併用しても0.1ppm程度までしか除去しえない。(しかもこの方法においては活性炭をかなり多量に添加するので、これによって活性炭中の不純物の溶出や濾過分離の際の活性炭の漏れなど多くの操作上の問題が派生する。)即ち、公知の脱砒素方法では何れの方法も燐酸液中の砒素含有量を0.01ppm迄低下させることは不可能であり、特に砒素含有量が数ppm以下の燐酸液においては、脱砒素率が非常に悪いというのが技術の水準であった。
【0008】本出願人等は、先にこの問題を解決する方法を種々模索する中で、燐酸液の砒素含有量によって砒素除去率が異なる点に着目し、燐酸液に、粉状の無機砒素化合物を添加した後、砒素除去を行う方法を試みた処、砒素含有量の低い場合は公知の方法では何れも脱砒素後の砒素含有量を0.01ppm以下迄除去しえなかったにもかかわらず、無機砒素化合物を微量添加することにより何れの燐酸についても砒素含有量を0.01ppm以下になしうると言う結果を得、提案した(特公昭58－46445号公報)。
【0009】しかし、この方法は、砒素の除去については有用であるものの、新たに無機の砒素化合物を添加する必要があることや、処理せしめた砒素分を含む硫化物の処理等、解決すべき問題点があり、更なる改善が望まれていた。
【0010】
【課題を解決するための手段】そこで本発明者等は、硫化水素ガスと砒素との反応、及び活性炭による吸着除去につき、再度、種々研究を重ねた結果、燐酸液に硫化水素ガスを添加し、反応せしめた後、活性炭にて、反応生成物を吸着除去する方法を見いだし、本発明の完成に至ったものである。
【0011】即ち、本発明は燐酸液中の砒素を硫化水素ガスと反応させて、該燐酸液中の砒素を硫化物として除去する方法において、温度が30～80°Cの燐酸液中へ、該燐酸液中の砒素分に対して重量比にて30倍～150倍の硫化水素ガスを予め分散し、反応せしめた後、石炭系活性炭を充填した活性炭塔にて、反応生成物である硫化物分を吸着除去することを特徴とする燐酸液の精製法である。更には、用いる活性炭が、粒状炭である、また、処理しようとする燐酸液の濃度がP_2O_5濃度として35～56重量%(以下%は全て重量%を表す)である前記燐酸液の精製法である。

【0012】本発明を更に詳細に説明する。砒素の除去を行う際、酸性条件下にて、硫化水素を生成する化合物は前述の如く数多くの化合物があるが、処理しようとする燐酸液への影響を考慮した場合、カチオンの影響のない硫化水素ガスが好適である。
【0013】該硫化水素ガスの添加量としては、燐酸中の砒素分に対し重量比にて30倍～150倍(As:H2S＝1:30～150)、好ましくは、50倍～120倍、更に好ましくは、60倍～100倍である。硫化水素ガスの添加量が30倍以下であれば、本発明者等の研究によれば、脱砒素の低下を招き、処理後の燐酸液中の砒素濃度が0．01ppm以下をクリアーすることが出来ない。また150倍以上であれば脱砒素の効果は問題のないものの、活性炭に硫化水素ガスが吸着されるため、活性炭の寿命の低下を招くと共に、硫化水素ガスによる用いる金属材料の腐食の問題もあり、好ましくない。
【0014】この様に、燐酸中の砒素分の除去については、硫化物としての理論値に対して大過剰量の硫化水素ガスを添加せしめることで、本発明の効果を達することが出来るものである。
【0015】本発明の方法が有効な燐酸液は乾式、湿式、抽出の何れの燐酸液でも良い。本発明での燐酸液の濃度としては、P_2O_5濃度として35～56%、好ましくは、40～50%である。P_2O_5濃度35%以下では、処理しようとする燐酸液の容量が多くなり、工業的に好適でなく、また本発明者等の研究によれば、脱砒素の効果も充分発揮出来ない。逆に、P_2O_5濃度56%以上であれば、燐酸液の粘度の上昇があるため、活性炭への吸着能の低下がみられ、好適でない。
【0016】処理しようとする燐酸液中の砒素の含有量としては、数ppm程度が好適である。それ以上の場合においても、本発明の効果は充分実証可能であるが、経済的には、従来の方法にて、予め数ppm程度迄脱砒素を行った後、本発明の方法を用いることが、有用で効率的ある。
【0017】また、反応温度(燐酸液温度)としては、30～80°C、好ましくは40～60°Cである。温度30°C以下では硫化水素ガスと砒素との反応が不十分で、更に燐酸液の粘度が上昇するためか、活性炭への吸着能の低下がみられる。80°C以上の場合は、硫化水素ガスによる装置への腐食の問題があり、用いる材質をより高級なものにする必要があるとともに、温度を維持するためエネルギーが必要となり、経済的でない。
【0018】活性炭としては、粒状、粉状活性炭いずれでも本発明の効果の面においては問題はないものの、再生が容易に可能なこと、塔に充填し処理しようとする液を通過せしめることで、その効果が得られることから、粒状活性炭が好適である。活性炭の種類としては、その原料ソースから、石炭系、椰子殻系、ピッチ系、木炭系があるが、脱砒素の効果から判断すれば石炭系が好適である。
【0019】本発明の方法は回分方法及び連続法のいずれの方式でも実施することができるが、連続法の方が通常は操業が容易である。
【0020】以下、本発明の好適な一実施例を、添付せる図面を参照しながら詳細に説明する。図1は、本発明の実施の好適な一態様を示すフローシートである。
【0021】燐酸液1は、ミキサー2にて所定量の硫化水素ガス3を添加し、該燐酸液中に均一に硫化水素ガス3を分散せしめる。ミキサー2は、硫化水素ガスを燐酸液中に極短時間に、均一に分散せしめる形式のものが好ましく、例えばラインミキサー等が好適である。
【0022】硫化水素ガスと燐酸液の接触時間、即ち反応時間は特に限定するものではなく充分均一に、気液が接触する条件であれば、極めて短時間でよく、例えば秒単位でも特に問題はない。
【0023】次に、硫化水素ガスを添加し処理せしめた燐酸液4は、石炭系でかつ粒状活性炭を充填した活性炭塔5に導き、硫化物を吸着除去せしめた脱砒素燐酸液6を得る。
【0024】活性炭塔5における、粒状炭の粒径としては、塔の圧力損失及び吸着効率を鑑みて、0．4～2．0mm程度(平均粒径0．9－1．1mm程度)のものが好適であり、燐酸液の通液速度としては、処理しようとする燐酸液の砒素を除く不純物分の含有量を考慮する必要があるが、0．5～2．0m／h程度にて通液すると良い。尚、用いる活性炭の物性としては、一般に市販されている液相用活性炭で充分であり、BET法による比表面積900～1300m^2／g、ヨウ素吸着量900～1100mg／g、細孔容積0．9～1．0cc／g程度の物性のものであれば、特に限定はない。
【0025】
【実施例】以下、実施例及び比較例によって、本発明の効果を具体的に説明する。
【0026】実施例1表1に示す組成の乾式燐酸液を用いて、図1のフローに従って、連続的に試験を実施した。尚試験時間は150時間行った。

【0027】
【表1】

P_2O_5	42～43%
As	2.0 ～2.5ppm

【0028】ラインミキサーを用いて、温度50～53℃の燐酸液3．5t／hに硫化水素ガスを440g／h添加し、次いで石炭系の粒状活性炭（東洋カルゴン社製、商品名F－400）15m^3を充填した活性炭塔（塔径2．0m）を通過せしめた後、燐酸液中の砒素を10時間毎に分析したところ、砒素濃度は全て0．01ppm以下であった。
【0029】比較例1硫化水素ガスを添加しない以外は実施例1と全く同様の操作を行った結果、燐酸液中の砒素濃度は10時間毎の測定において、0．10～0．15ppmであった。
【0030】比較例2実施例1と同様な方法で硫化砒素ガスを40g／h添加し、同様の試験を行った。燐酸液中の砒素濃度は10時間毎の測定において0．10～0．13ppmであった。
【0031】実施例2表2に示す湿式法にて得られた燐酸液を、用いて実施例1と同様連続試験を実施した。連続試験時間は120時間実施した。
【0032】
【表2】

P_2O_5	50～53%
有機物（as C）	60～80ppm
As	0.05～0.10ppm

【0033】ラインミキサーを用いて、温度40～45℃の燐酸液5．0t／hに硫化水素ガスを25g／h添加し、次いで石炭系の粒状活性炭（東洋カルゴン社製、商品名F－400）15m^3を充填した、活性炭塔（塔径2．0m）を通過せしめた後、燐酸液中の砒素を10時間毎に分析したところ、砒素濃度は全て0．01ppm以下であった。
【0034】比較例3燐酸液の温度を20～25°C、それ以外は実施例2と全く同様の操作を行った結果、燐酸液中の砒素濃度は10時間毎の測定において、0．04～0．07ppmであった。
【0035】比較例4粒状活性炭を椰子殻炭（三協産業社製ダイヤソーブW）に入れ替えた以外は全く実施例2と同様の実験を行ったところ、燐酸液中の砒素濃度は10時間毎の測定において、0．05～0．08ppmであった。
【0036】
【発明の効果】本発明は、従来使用しなければならなかった新たな無機砒素化合物を添加せずに、0．01ppm以下まで砒素を除去することが可能であり、工業上極めて有用なものである。
【0037】本発明の燐酸液の精製方法は、前述の如く1）予め処理しようとする燐酸液へ硫化水素ガスを添加し、液中に分散せしめる気液接触工程、及び2）活性炭を充填せしめた活性炭塔からなる吸着工程で充分であり、極めて簡単な方法及び設備にて除去出来ることも本発明の特徴である。またこの活性炭塔5は、その他、例えば有機物の除去や製品の脱色あるいは、その他重金属や金属分の除去等も、同時に実施することが出来、既存の設備をもちいて、活性炭銘柄の変更あるいは、混合使用

等にて処理できることも、本発明の特徴の一つである。また別途新たに本発明における装置を設置する場合においても、簡単な装置を設けるだけで良く、建設コストも極めて安価に対応出来るものである。

【0038】特に砒素含有量が数ppm以下の燐酸液からの更なる脱砒素においては、本発明の方法は従来公知の方法に対して、極めて格段に優れた効果を示す点が注目すべきである。

図の説明

【図面の簡単な説明】

【図1】本発明を実施するために適した装置の一例を示すフローシート図

【符号の説明】

1 燐酸液
2 ミキサー
3 硫化水素ガス
4 硫化水素ガスにて処理した燐酸液
5 活性炭塔
6 脱砒素燐酸液

図面

【図1】